5.1 PRODUCTION



Prior to the public's outcry concerning the apparent link between PCBs and widespread environmental problems and the discovery of their detrimental health effects, PCBs were produced commercially in the United States from 1929 until 1977. Marketed worldwide under trade names such as Aroclor, Askarel, and Therminol, the annual U.S. production peaked in 1970 with a total production volume of 85 million pounds (39 million kg) of Aroclors. Between 1957 and 1971, 12 different types of Aroclors, with chlorine contents ranging from 21 to 68% were produced in the United States. The manufacturing process for Aroclors involved the chlorination of biphenyl with anhydrous chlorine in the presence of a catalyst, such as iron filings or ferric chloride. The degree of chlorination, which determines the nature of the Aroclor, was controlled by the chlorine-contact time (range, 12-36 hours) in the reactor. Late production Aroclor 1254 (Aroclor 1254 "Late") was made by a two-stage chlorination procedure from 1974 to 1977. In the first stage, biphenyl was chlorinated to 42% chlorine content by weight as for Aroclor 1242 production. This was then fractionated to give a distillate that was sold as Aroclor 1016 and a residue that would have contained mostly the mono-ortho tetrachlorobiphenyls and higher homologs. In the second stage, this residue, which contained about 49% chlorine, was further chlorinated to 54% chlorine by weight, resulting in an Aroclor 1254 lot (Monsanto Lot KI-02-6024) with greatly increased levels of the high TEF (i.e., 2,3,7,8-tetrachlorodibenzo-p-dioxin ("dioxin") Equivalency Factor; "T" often defined as "toxic") chlorobiphenyls. While production records suggest that Aroclor 1254 "Late" represented <1% of the total Aroclor 1254 production, the availability of this lot during the final years of production resulted in the disproportionate use of Aroclor 1254 "Late" by standards suppliers and researchers into Aroclor 1254 toxicity (Brinkman et al. 1995; Durfee 1976; Frame 1999; IARC 1978).

During production, Aroclor mixtures were contaminated by small amounts of polychlorinated dibenzofurans (PCDFs) as impurities. Although PCDFs are formed during the pyrolysis of PCBs, in the absence of fire, PCDF levels do not appear to increase during the normal use of PCBs in electrical equipment. PCDFs have their own toxicological properties, which have been summarized in ATSDR (1994). The concentration levels for tetra-, penta-, hexa-, and total PCDFs found in commercial PCB mixtures are shown in Table 4-6 (de Voogt and Brinkman 1989).

Approximately 99% of the PCBs used by U.S. industry were produced by the Monsanto Chemical Company in Sauget, Illinois, until production was stopped in August 1977. Prior to 1971, the Monsanto

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL
Chemical Company produced Aroclors 1221, 1232, 1242, 1248, 1254, 1260, 1262, and 1268; however, in

1971, the company voluntarily restricted the uses of PCBs and subsequently produced only Aroclor 1016, 1242, 1254, and small quantities of Aroclor 1221. In 1974, the Monsanto Chemical Company produced slightly more than 40 million pounds (18 million kg) of Aroclor mixtures. Of the total volume of Aroclors sold in the United States for that year, the percentages of the market for each of the Aroclors were: Aroclor 1016, 64%; Aroclor 1242, 17.9%; Aroclor 1254, 17.9%; and Aroclor 1221, 0.1%. The estimated, cumulative production and consumption volumes (in millions of pounds) of PCBs in the United States from 1930 to 1975 were: total production, 1,400 (635 million kg); imports, 3 (1.4 million kg); domestic sales, 1,253 (568 million kg); and exports, 150 (68 million kg). Section 5.3 provides information on amounts estimated for specific locations, as well as estimates of intermedia transfers of PCBs (Durfee 1976; EPA 1976a; Hatton 1979; IARC 1978; Kimbrough 1987).

In 1976, the U.S. Congress charged EPA with regulating the manufacture, processing, distribution in commerce, and use of PCBs. Currently regulated pursuant to the Toxic Substances Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA), the first set of effluent standards for PCBs was issued by EPA in 1977; manufacturing and importing limitations regarding PCBs were issued in 1979. After subsequent amendments, the regulations stipulate that the production of PCBs in the United States is generally banned, the use of PCB-containing materials still in service is restricted, the discharge of PCB-containing effluents is prohibited, the disposal of materials contaminated by PCBs is regulated, and the import or export of PCBs is only permitted through an exemption granted from EPA (EPA 1977b, 1979a, 1979f, 1979g, 1988c, 1988e, 1998a).

5.2 IMPORT/EXPORT

Currently, the United States neither imports nor exports PCBs. Section 6(e)(3)(A) of TSCA (Pub. L. 94-969, 90 stat. 2003, 15 USC 2601 et. seq.) prohibited all manufacture and importation of PCBs after January 1, 1979. On January 2, 1979, however, EPA announced that companies that had filed petitions for exemptions from the PCB manufacturing/importation ban could continue manufacturing or import activity until EPA acted on the application petition. As of July 7, 1997, the U.S. Court of Appeals for the Ninth Circuit overturned the Import for Disposal Rule. EPA can now only allow imports of PCBs by issuing exemptions to importers via the petition process under Section 6(e) of TSCA. See the June 29, 1998 Federal Register for further discussion of EPA's PCB export and import regulations (EPA 1979a, 1998a).

In 1973 and 1974, the United States imported PCBs mainly from Italy as decachlorobiphenyl (Fenclor), and France (Phenoclor) (Durfee 1976). It is estimated that 180,000 kg (approximately 400,000 pounds) of this compound were imported in 1974 (IARC 1978). The volume of PCBs imported through principal U.S. custom districts from unspecified countries decreased from 132,000 kg (291,000 pounds) in 1976 (IARC 1978) and 280,867 pounds (127,400 kg) in 1977 to only 11,000 pounds (5,000 kg) in 1981 (USITC 1978, 1979, 1980, 1982). The Monsanto Chemical Company exported 5.4 million pounds (2.45 million kg) of Aroclors 1016 and 1242 to unspecified countries in 1974 (Durfee 1976).

5.3 USE

Prior to 1974, PCBs were used both for nominally closed applications (e.g., capacitor and transformers, and heat transfer and hydraulic fluids) and in open-end applications (e.g., flame retardants, inks, adhesives, microencapsulation of dyes for carbonless duplicating paper, paints, pesticide extenders, plasticizers, polyolefin catalyst carriers, slide-mounting mediums for microscopes, surface coatings, wire insulators, and metal coatings) (Durfee 1976; EPA 1976a, 1988c; IARC 1978; Orris et al. 1986; Safe 1984; Welsh 1995). Table 5-1 summarizes the former uses of the various Aroclors. Currently, under 40 CFR 761.80 (June 29, 1998), individual petitioners are granted 1-year exemptions to manufacture or import PCB for use solely in the manufacture or importer's own research for the development of PCB disposal technologies. Also under 40 CFR 761.30 (June 29, 1998), individual petitioners are granted exemptions for the use of PCBs as a mounting medium in microscopy, as an immersion oil in low fluorescence microscopy, and as an optical liquid, as well as for analytical samples and research and development use (EPA 1998a).

Except for the approximate 400,000 pounds (180,000 kg) of decachlorobiphenyl imported from Italy and France used as filler for investment casting waxes (IARC 1978), most domestic use of PCBs was restricted to nominally closed applications by 1974 (IARC 1978). The production of capacitors and transformers involved filling them with Aroclors through a small hole in the unit and then sealing the hole. While smaller capacitors contained smaller amounts, the production of large capacitors generally required at least 2–3 pounds (1 kg) of Aroclors; many times that amount was required to produce the transformers. By 1976, only 5% of the transformers produced in the United States were filled with PCBs, accounting for 30% of the Monsanto Chemical Company's domestic sales; however, 95% of the capacitors produced in the United States were filled with PCBs, accounting for 70% of the company's domestic sales (IARC 1978). As of January 1979, Aroclors were no longer used in the production of capacitors and transformers. Nevertheless, the life expectancy of transformers containing PCBs is greater

 Table 5-1. Summary of Former End Uses for Various Aroclors

		Aroclor								
End use	1016	1221	1232	1242	1248	1254	1260	1262	1268	
Capacitors		• ,		· .		•				
Transformers	-	T.		•		•	•			
Heat transfer				•						
Hydraulics/lubricants										
Hydraulic fluids			•	•	•	•	•			
Vacuum pumps					•	•				
Gas-transmission turbines		•		•						
Plasticizers:					•					
Rubbers		•	•	•	•	•			•	
Synthetic resins				٠	•	•	•	•	•	
Carbonless paper				•			•			
Miscellaneous:				•						
Adhesives		•		•	•	•				
Wax extenders				•		•			•	
Dedusting agents						•	•			
Inks	•					•				
Cutting oils						•	,	•		
Pesticide extenders						•				
Sealants and caulking compounds						•				

Source: IARC 1979

than 30 years, and the life expectancy of capacitors ranges from 10 to 20 years, depending on the electrical application (IARC 1978). In 1981, an estimated 131,200 transformers containing PCBs were in service in the United States, representing approximately 1% of all operational transformers. Currently, the EPA maintains an up-to-date database containing the location and amount of PCBs in transformers across the United States (EPA 1999b).

5.4 DISPOSAL

According to the Toxics Release Inventory (TRI), >99% of the total PCB wastes produced in the United States in 1998 were released on-site to land. About 3,742,000 pounds (1,698,000 kg) of PCB wastes were released to land in 1998 (see Table 5-2) (TRI98 2000).

The concentration of PCBs in the environment in which some action should be considered (i.e., treatment or containment) will depend primarily on the exposure estimate determined during the baseline risk assessment for the site and on EPA's 1996 cancer slope factor, reference dose (RfD), and exposure-specific values (EPA 1990e, 1996c).

PCBs were included among the contaminants of concern at 500 of the 1,598 Superfund sites (29%) as of May 11, 2000 which were listed on the Final National Priorities List (HazDat 2000). Remedial actions taken at Superfund sites must meet the mandates of the National Contingency Plan (NCP), which implements the requirements of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) (EPA 1990e). CERCLA Section 121 provides specific statutory requirements (cleanup standards) for remediation that must be addressed when evaluating proposed remedial alternatives (U.S. Congress 1980). In order to ensure that the statutory requirements are met, the various proposed alternatives are evaluated using nine evaluation criteria that reflect these statutory requirements (U.S. Congress 1980; EPA 1988j, 1989d, 1990e). The nine criteria are categorized into three groups: threshold criteria, primary balancing criteria, and modifying criteria. The threshold criteria include the requirements to provide overall protection of human health and the environment, and to comply with applicable or relevant and appropriate (ARARs) federal and state laws (EPA 1988j, 1989d). The primary balancing criteria include provisions for evaluating long-term effectiveness and permanence; the reduction of contaminant toxicity, mobility, or volume; and short-term effectiveness for adverse health effects from human exposure, implementability, and cost. The modifying criteria include state acceptance and community acceptance (EPA 1988j, 1989d). While the primary balancing criteria are used to weigh major tradeoffs among the proposed alternatives, and the modifying criteria are not taken into account

Table 5-2. Facilities that Manufacture or Process Polychlorinated Biphenyls

Facility	Location	Range of maximum amounts on-site in pounds	Activities and uses		
Norcross Safety Prods. L.L.C.	Rock Island, Illinois	100–999	Produce, by-product		
Unison Transformer Services	Henderson, Kentucky	1,000–9,999	Ancillary/other use		
Noranda Aluminum Ínc.	New Madrid, Missouri	10,000–99,999	Ancillary/other use		
Special Metals Corp.	New Hartford, New York	10,000–99,999	Ancillary/other use		
Northwest Aluminum Co., Inc.	The Dalles, Oregon	10,000–99,999	Ancillary/other use		

Source: TRI96 1998

until after public comments are received on the proposed remediation plans, an alternative must satisfy the threshold criteria in order to be eligible for selection (EPA 1988j, 1989d).

On April 18, 1978, EPA began to regulate the storage and disposal of PCBs. These regulations specified incineration as the only acceptable method of PCB disposal unless, by reason of the inability to dispose of the waste or contaminated materials in this manner, clearance was obtained from EPA to dispose of the materials in another way. Although in March 1983 EPA issued a procedural amendment to the PCB rule to enable new disposal technologies to receive approval on a nationwide basis, EPA's current PCB disposal rules generally require that PCBs at concentrations of • 50 ppm be disposed of in an incinerator approved for that use (EPA 1998u). The recommended combustion criteria for the disposal of liquid PCB wastes by incineration is a 2-second dwell time at 1,200 \cdot C ($\pm 100 \cdot$ C) and 3% excess oxygen in the stack gas; or a 1.5-second dwell time at 1,600 • € (±100 • €) and 2% excess oxygen (EPA 1979e). Since incineration of PCBs will produce chlorine-containing products (e.g., hydrochloric acid), it is required that water scrubbers be used to remove these products before releasing the emissions into the atmosphere (EPA 1998u). Under TSCA (Toxic Substance and Control Act), the combustion efficiency of the incinerator must be 99.9% (EPA 1998u). The general acceptance of incineration as a means of disposal for PCB-contaminated materials has declined because of concerns about incomplete incineration and the possible formation of highly toxic dioxins and dibenzofurans if the combustion temperature is not held sufficiently high (Arbon et al. 1994; Chuang et al. 1995). An evaluation of the applicability of oxy-fuel technology to waste incineration conducted by Baukal et al. (1994) reported favorable results. The test results indicated that for simulated soils containing 1% PCBs and oil containing up to 40% PCBs, more than 99.9999% of the PCBs were destroyed. In controlled experiments conducted by Chuang et al. (1995), significant dechlorination was noted at 300 • € and a fully dechlorinated product occurred at 400 • € when heating a mixture of PCBs (Aroclor 1221 and 1254) and iron metal powder (Fe⁰) in a muffle furnace.

The regulatory requirements implemented pursuant to TSCA also provide that chemical waste landfills and high-efficiency boilers meeting specified operating requirements are appropriate disposal facilities for mineral oil dielectric fluid from PCB-contaminated electrical equipment containing PCBs at concentrations • 50 ppm, but <500 ppm. Under the land disposal restrictions promulgated at 40 CFR part 268 pursuant to RCRA (Resource Conservation & Recovery Act), PCBs are regulated as halogenated organic compounds (HOCs). Types of waste for which land disposal is prohibited include liquid hazardous wastes containing PCBs at concentrations of • 50 ppm; nonliquid hazardous waste containing HOCs in total concentration greater than or equal to 1,000 mg/kg (ppm); and liquid HOC-containing

waste that are primarily water and contain HOCs in the concentration range 1,000–10,000 mg/L (ppm) HOCs. The treatment standards expressed as specified technologies (e.g., chemical reduction, carbon adsorption, biodegradation) require incineration of liquid hazardous waste containing PCBs at a concentration of 500 ppm or greater, and HOC-containing waste prohibited from land disposal (EPA 1986i, 1987c, 1987d, 1998u).

Although not widely adopted, other methods proposed for the destruction of PCBs have included wet air oxidation, biodegradation, metal-promoted dehalogenation, and electrolytic reduction (Chuang et al. 1995). Timberlake and Garbaciak (1995) detailed the results of a series of bench-scale tests applying various technologies (thermal desorption, solvent extraction, wet air oxidation, and an incineration process known as Anaerobic Thermal Process [ATP]) to PCB-contaminated sediment. The thermal desorption and solvent extraction technologies, though not designed to destroy the contaminants, indirectly separate the contaminants from a solid matrix and concentrate them into smaller volumes of treatable oily residues. The removal efficiencies of these technologies when applied to three of the river sediments tested ranged from 96 to 99%. The wet air oxidation process, which uses elevated temperatures and pressure to oxidize the organic constituents, was not very effective in destroying PCBs; it achieved only a 34% removal efficiency (Timberlake and Garbaciak 1995). Zhang and Rusling (1995) investigated electrochemical catalytic dechlorination as a method for decontaminating soils. The study achieved a 94% dechlorination level using a lead cathode and a micro emulsion of didodecylmethyl-ammonium bromide, dodecane, and water for soils containing 6.5% organic matter and contaminated with 14% Aroclor 1260 (84 mg of PCB).

A chemical destruction method that has been used for the treatment of PCBs in contaminated dielectric liquids or soil is based on the reaction of a polyethylene glycol/potassium hydroxide mixture with PCBs (De Filippis et al. 1997). This method can be used successfully for the destruction of higher chlorinated PCBs with an efficiency of >99%, but was found to be unsuitable for the treatment of di- and trichlorobiphenyls due to low destruction efficiencies (Sabata et al. 1993). Irradiation of PCBs in isooctane and transformer oil by γ-radiation resulted in degradation of PCBs to less chlorinated PCBs and PCB-solvent adducts (Arbon et al. 1996). Supercritical fluid technology has shown promise as a method for extraction of PCBs from soils, coupled with supercritical water oxidation of the extracted PCBs (Tavlarides 1993, 1998a). Hofelt and Shea (1997) demonstrated the use of semipermeable membrane devices to accumulate PCBs from New Bedford Harbor, Massachusetts water. Another method showing some promise for the treatment of PCBs in water, soil, and sediment is titanium dioxide-catalyzed photodecomposition with sunlight (Hong et al. 1998; Huang et al. 1996; Zhang and Rusling 1995; Zhang

et al. 1993). PCBs in used lubricating oils were destroyed and petroleum products, including lubricating oils, were produced with catalytic vacuum distillation/hydrotreatment technology (Brinkman et al. 1995). Treatment with metallic sodium has been suggested for PCB wastes because it yields low molecular weight polypropylene and sodium chloride which are less undesirable than products from incineration (IRPTC 1985). Bioremediation of PCB-contaminated soil has been suggested using a combination of anaerobic and aerobic treatments. Aerobic treatments would metabolize the lower chlorinated homologs (e.g., biphenyl; mono- and di-ortho chloro-substituted CBs) produced in soil from anaerobic dechlorination processes (Tiedje et al. 1993; see Section 6.3.2.3).